2013

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Zahra Poursharifi
Iowa State University

Maziar Ashuri
Iowa State University

Reza Montazami
Iowa State University, reza@iastate.edu

Nastaran Hashemi
Iowa State University, nastaran@iastate.edu

Proceedings of the ASME 2013 7th International Conference on Energy Sustainability & 11th Fuel Cell Science, Engineering and Technology Conference
ESFuelCell2013
July 14-19, 2013, Minneapolis, MN, USA

ES-FuelCell2013-18324

A NOVEL METHOD FOR FABRICATING CONDUCTIVE MICROFIBERS FOR MICROBIAL FUEL CELLS

Zahra Poursharifi
Department of Mechanical Engineering
Iowa State University
Ames, Iowa, United States

Maziar Ashuri
Department of Mechanical Engineering
Iowa State University
Ames, Iowa, United States

Reza Montazami
Department of Mechanical Engineering
Iowa State University
Ames, Iowa, United States

Nastaran Hashemi
Department of Mechanical Engineering
Iowa State University
Ames, Iowa, United States

ABSTRACT
The increasing demand for energy resources has urged scientists to focus on improving the renewable energy sources. Microbial fuel cells (MFCs) have received an increasing attention. Both energy conversion mechanism and electrode type have attributed to affect the efficiency of the microbial fuel cells. Electrodes as one of the most important components of the microbial fuel cells have been widely investigated. While most of the electrode materials are carbon based, there is very little effort on introducing novel materials for this purpose. This paper intends to shed an insight on the effect of using a new cathode material on the performance of microbial fuel cells. We employ hydrodynamic forces to control both molecular organization and microstructure size and shape in order to create highly structured microfibers. A microfluidic sheath flow device is used for the fabrication processes. The core flow is acrylate solution and UV light cures the photoinitiator to start the polymerization process. The exiting stream goes inside a water bath, where the sheath flow dissolves in the DI water and the core flow forms the microfibers. Controlled self-assembly can be used to deposit a thin layer of functionalized metal nanoparticles on the polymeric structure made from microfibers to enhance their electric conductivity. A conductive and porous network formed by the microfibers can be used as an efficient cathode material in microbial fuel cells. Furthermore, using this fabrication technique we can make microfibers with different shapes and sizes.

INTRODUCTION
Devices utilized for creating and storing energy have received increasing attention in recent years. And the electrode specifications is a factor strongly connected. A vast variety of materials are being introduced to be utilized as the electrode part material.
In recent years, the scientific investigation process related to the supercapacitors as energy storage devices has undergone a significant evolution, due to the great advantages of super capacitors in storing and releasing energy at high rates [1]. Accordingly, there have been immense advances in the field of capacitors, especially for improving the performance of electrodes. In this regard, many novel materials have been introduced as the electrode components. The polypyrole has been utilized as a conducting polymer electrode for electrochemical redox supercapacitors [2]. Furthermore, multi-walled chemically activated carbon nanotubes were used as the material which provides a better conductivity for the supercapacitor electrodes [3]. As an innovative concept, Nickel and Cobalt chemically synthesized oxide composites has been introduced as a possible electrode material in the field of electrochemical supercapacitors [4]. Nanoporous carbon black particles which are fabricated through the mechanical pressing method, has been mentioned as a low cost electrode material for being utilized in electrochemical double layer capacitors [5]. A large amount of work has been carried out on investigating carbon and its derivitives as high quality conductive electrodes in energy applications. graphene nanosheet/carbon nanotube/polyaniline composite are utilized as electrode material for supercapacitors to increase the cycle

stability due to the high conductivity as well as high mechanical strength of the electrode [6]. Among the different types of materials introduced for electrode material, the nanoporous metal, which is manufactured by plating conductive polypyrole into channels of a dealloyed nanoporous metal, have been reported to be a desired type of electrode for pseudocapacitors by supporting the two important specifications of low electric resistance and high porosity [7].
In past years, many investigations have been carried out to study the materials utilized in the electrode part of the batteries, with special focusing on the Lithium-Ion batteries. Poly(3,4-ethylendioxythiophene) PEDOT-LiFe Po_4 film is introduced as the positive electrode in lithium- Ion batteries. These films are manufactured by dynamic three phase interline electropolymerization method. The most significant approach of this material is conductivity as well as the fact that size and structure can be specified [8]. A novel designed Cu/Super-P composite has been introduced. This material is utilized in the anode part of the lithium- Ion batteries [9]. Furthermore, $LiFePo_4$-Fe_2P-C composites have been introduced as cathode electrode which provides high porosity as well as high conductivity for lithium-ion batteries [10]. Multi-walled carbon nanotubes, have been introduced as a viable alternative for the conductive material added for improving the performance of lithium-ion batteries. The nanotubes produced by the chemical vapor deposition method, result in increasing the energy and power densities of the battery [11]. By electrospinning a solution of polyacrylonitrile and polypyrrole, carbon nanofibers are fabricated for being utilized in the anode part of the rechargeable lithium-ion batteries. These nanofibers are consequently carbonized in high temperature. The significant feature of this material is improving the electrochemical performance due to their specific surface pattern, which provides an easy path for electrons to move [12].

Many research has been focused on the solar energy as a viable energy source. In this regard, novel structures and materials are being introduced in this field as well. N79 dye-synthesized TiO_2 nanotubes /Ti wire is used as the working electrode in the needle-shaped three dimensional dye- synthesized solar cells. It has been concluded that Pt nanoparticle/carbon fiber demonstrates higher efficiency in comparison with Pt wire [13]. Hybrid electrodes, consisted of multi-walled carbon nanotubes and are presented to have improved performance characteristics. These types of electrodes are fabricated through a solution-based method. They exhibit lower internal resistance as well as lower resistance to diffusion. These specifications are due to the porosity of the hybrid electrodes structure [14]. A recent study proposed that, flexible metal-free fibrous electrodes exhibit significant performance as the electrodes of the dye-synthesized solar cells. These electrodes are fabricated by utilizing carbon fiber and poly(3,4-ethylene dioxythiophene)-polystyrene sulforate(PEDOT:PSS) solution. Furthermore, they present higher energy conversion efficiency [15].

Scientists have expanded the scope of this research to diverse zones such as fuel cells. Carbonaceous materials are the dominant material utilized in the composition of electrodes for Microbial fuel cells. These materials have several advantages such as being highly conductive, biocompatible and stable [16]. Carbonaceous materials in the form of plane structure are mostly used in the forms of carbon cloth and carbon papers [17]. In order to expand the electrode available surface area, packed structure is introduced for the MFCs anode part [18]. Furthermore, for a more increase in the porosity amount of the electrode material as well as the conductivity, carbon brush structure is introduced. However this material is disadvantageous because it blocks the access of bacteria to the surface area [19]. In several cases, metal based materials specifically stainless steel is used as the electrode material for the MFCs [20]. Furthermore, Titanium is commonly used as the anode material for the MFC electrode [21]. It should be mentioned that gold anodes have been investigated as MFC electrodes [22-23]. Also, Metal-graphite composite anodes have been investigated as an alternative anode material for improving power generation performance of MFCs [24-25].A novel design for the anode electrode of microbial fuel cell is introduced by fabricating electrochemically reduced graphene oxide which is coated with poly aniline nanofibers on the surface of the carbon cloth. High conductivity and greater surface area are the two key parameters which improve the microbial fuel cell anode performance [26]. CNT–textile–Pt composite are one of the novel materials which are designed as an aqueous-cathode of the MFC, which has led to a significant improvement in the power generation process [27]. Furthermore, three dimensional CNT-textile utilized as the anode part of the microbial fuel cell has been effective in improving the performance from the viewpoints of higher current, higher power density and higher energy recovery. This material provides an open space for an effective interaction of biofilm [28].
In the case of methanol fuel cells, Silver has been proposed as electrode material for miniature direct methanol fuel cells. The silver base electrodes, support high thermal and electrical conductivity and they have acceptable resistance against corrosion [29]. In the present paper, a novel method has been introduced for fabricating high conductive and porous microfibers as the electrode material for energy applications. To this end a microfluidic sheath device with a specific geometry has been utilized. The core and the sheath flow are controlled by syringe pump. The core flow is composed of acrylate and the polymerization starts as the UV light cures the photoinitiator. The flow immediately enters the water bath, where the sheath flow dissolves in the DI water and the components of the core flow build the microfibers. Once the microfibers are fabricated, they have the possibility to be coated by gold nanoparticles to become conductive. These microfibers can have two key advantages including high porosity and high conductivity.

EXPERIMENTL PROCEDURE

A microchannel with four chevron-type grooves was utilized for fabricating highly porous microfibers. The channel has a symmetric geometry with a single core inlet and two entries for the sheath flow [30-31]. The channel is made in two halves of PDMS (Polydimethylsiloxane), the transparent nature of the PDMS chamber makes the UV light (Dymax Corporation, Torrington, CT) transmit through the channel. UV light is utilized for initiating the polymerization process. Accordingly its head is adjusted after the chevrons where the fluid flow has been focused completely.

For implementing the hydrodynamic shaping of the microfibers, the chamber is located vertically on the surface of the water bath. The manufactured fibers accompanied with the sheath flow enter the water bath directly, where the sheath flow dissolves inside the water and the fibers are collected around a miniature frame. A double syringe pump (Cole-Parmer, VeronHillss, IL) was utilized for supporting the 10 $\mu Lmin^{-1}$ flow rate for the core flow and 200 $\mu Lmin^{-1}$flow rate for the sheath flow.

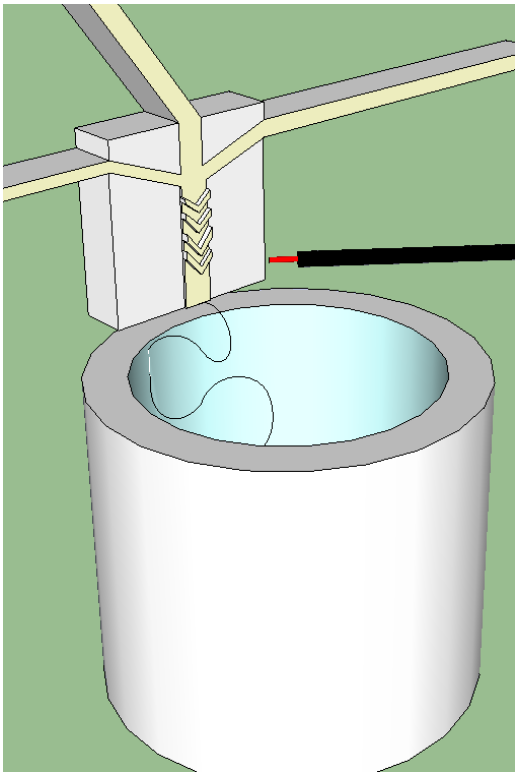


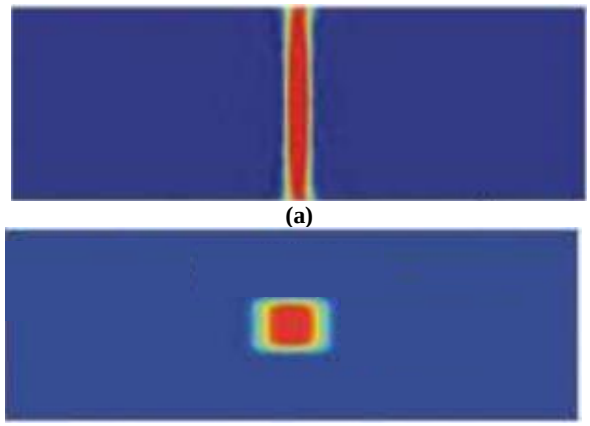
Fig.1. Schematic figure of the experimental setup.

The chemical combination utilized for preparing the sheath flow are as follows: glycerol (50 v%), methanol (25 v%) and water (25 v%). Moreover, the following components were mixed for fabricating the core flow: 4-hydroxybutyl acrylate (85 wt%), acrylic acid (11 wt%) diluted at a stock concentration of 1 µL in 1 mL of water, photoinitiator which was dissolved in dichloromethane (3 wt%) and ethylene glycol dimethacrylate (1 wt%).

All the chemical materials were purchased from Sigma-Aldrich. After all the components were mixed together, they were poured through the inhibitor removal column [32]. Schematic figure of the experimental setup is shown in Fig. 1. In this figure, the channel inlets are depicted with yellow color. The UV light is probe is depicted by black tube, and the UV shine is schematically shown by the red color.

RESULTS AND DISCUSSION

We have used COMSOL Multiphysics software to simulate the core flow pattern inside the microchannel. Fig2.a. represents the core flow pattern as it enters the channel. It should be mentioned that the simulations has been carried out for the quarter of the channel in order to reduce the computational time. It is obvious from the figure that, the core flow is horizontally focused by the sheath flow. Fig 2.b. represents the core flow pattern after the last chevron. It is obvious from the figure that, an extra vertical compression has been applied to the core flow by the chevrons. The core flow rate is 10 $\mu Lmin^{-1}$ and the sheath flow rate is 200 $\mu Lmin^{-1}$.



(a)

(b)

Fig.2. COMSOL Multiphysics simulations of the core flow pattern at a sheath to core flow rate ratio of 200:10. (a) Core flow pattern at the channel entrance. (b) Core flow pattern after the last chevron.

The mechanism through which these microfibers are manufactured is mainly dependent on the configuration of chevrons which focus the core flow in a simultaneous procedure through which the core flow is mainly surrounded by the shear flow to have the least contact with the walls of the channel. The SEM image from the manufactured microfibers is presented in Fig.3. These microfibers can be woven together to create a porous network. The network's inherent porosity can provide a suitable environment for bacteria to attach and grow. It also facilitates the penetration of nutrient solutions (fluids) into the pores. This method has several advantages as it provides a porous area, So that bacteria can attach to its surface easily and grow on it. Furthermore, the high potential of these fibers to become conductive through conventional and easy

processes highlights their ability to perform as the electrode part of the microbial fuel cells. If the manufactured microfibers are embedded in a pool of conductive metal nanoparticles such as gold nanoparticles, these nanoparticles would attach the surface of the microfibers supporting the adequate conductivity required for an electrode. It is worth mentioning that, the manufactured fibers are being collected by the operator through the manufacturing process, so it is possible to align them in arbitrary designs.

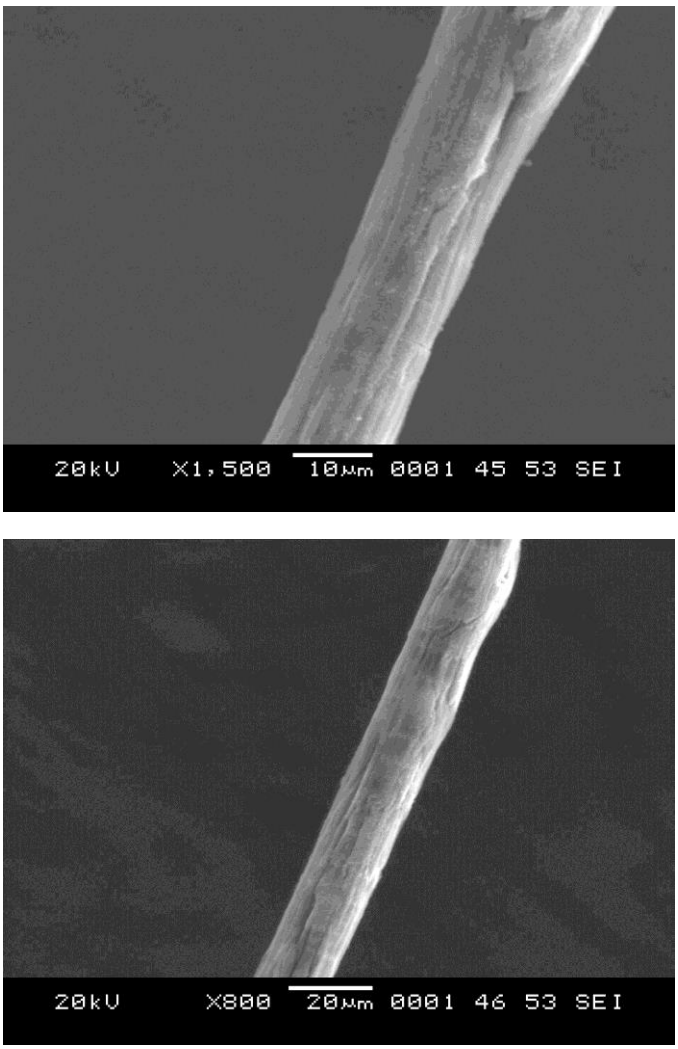


Fig.3. SEM images of fabricated microfibers.

In this study, as mentioned in the experimental procedure part, we collected the microfibers on a window, However they can also be collected on a folded surface, and by unfolding the surface we can have a series of aligned microfibers in the form of a smooth layer. This important feature of the mentioned method can be useful for making scaffolds or microfiber textures. There are several papers in technical literature that have used this method in a reverse operating mode. It means that they have manufactured a hollow microfiber of the sheath flow, as the core flow dissolves inside the water bath. The hollow fibers have extensive application in cell growth.

CONCLUSION

In the present paper, a novel approach is introduced for fabrication of highly conductive and porous microfibers to be positioned as the electrode part of the microbial fuel cells. A microchannel with chevron groove design is utilized for this purpose. The microfibers are formed as the sheath flow surrounds the core flow while the chevrons focus it in the middle of the channel. The suggested method of this paper for making the microfibers conductive is to coat them with nanoparticles [33-34]. Therefore, they will have the two key parameters of porosity and conductivity for supporting the bacteria attachment and conducting the electric currency, respectively.

ACKNOWLEDGMENTS

We would like to acknowledge the support provided by the William March Scholar Fund and the Iowa State University Foundation. We also thank Pouya Asrar for assisting us in COMSOL simulations.

NOMENCLATURE

MFC	Microbial Fuel Cell
DI	Deionized

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